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Paint Formulation Using Water Based Binder and Property Studies

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Summary: Vinyl acetate – Butyl acrylate (VAc-BuA) copolymer latices of various compositions were prepared by semicontinuous emulsion polymerization. The copolymer formed after removing the homopolymers was characterized by FTIR spectroscopy. Mechanical properties were studied by Universal Testing machine. Differential scanning calorimetry (DSC) study of copolymer showed single glass transition temperature (Tg) value confirming the absensce of graft and block copolymer. These copolymer latices were used as the binder in water based latex paint formulation. The paint prepared using 85/15 wt.% of VAc-BuA was found to give a better paint properties. Water based paints are generally easier to apply and clean up. The surface properties found to be superior compared to commercially used paint.

Keywords: copolymer; DSC; emulsion polymerization; FTIR; lattices

Introduction

In recent years there has been a considerable change in the coating industry. Architectural paints are mainly used for decoration, but also play a serious role in protecting our major assets from natural weathering process. To create a quality of paint, quality raw materials are essential. The property of the paint is determined by the quality of binder. The binder is the most important raw material that affects almost all properties of coating. The final conversion of film to durable coating takes place by curing and drying process depending on the nature of the polymer. Polyvinyl acetate widely used as a binder suffers poor hydrolytic stability especially under alkaline condition, poor weathering stability, poor wet adhesion and high water sensitivity.[1] It has only limited application in exterior coating because of the high Tg (30 °C) and minimum film forming temperature (MFT) 20 °C making its film too hard and inflexibility limiting its use in paint application. So vinyl acetate polymerized with butyl acrylate substantially improves the glass transition temperature of the film.[1] Vinyl acetate-Butyl acrylate copolymer, prepared via semicontinuous emulsion polymerization has better film forming property. The important properties of emulsion polymers are total solid content, pH, viscosity, particle size, glass transition temperature and chemical composition. The homogeneity of copolymer composition within the particle is expected to be a strong function of monomer composition in the feed and method of monomer addition. Lower solid content emulsion is preferable than high solid content emulsion for a better performance.[2] The VAc-BuA system is well known as low volatile organic content (VOC) binder for typical paint application. This paper describes a method for preparing a binder based on VAc and BuA and subsequent characterisation of the binder and thereby develops new paint formulation.

Experimental Part

Materials Used

Both monomers, Vinyl acetate (VAc) and n-butyl acrylate (BuA), were purchased

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from Loba chemie Pvt. Ltd. and were distilled under vacuum to remove the inhibiter. Doubly deionized (DDI) water was used in all polymerization. Ammonium persulphate and sodium carbonate were AR grade obtained from Merck. Sodium dodecyl benzene sulphonic acid (HPLC grade) from Loba chemie Pvt.Ltd. and Rexol (N-300) from Laffans petrochemicals limited were used.

Preparation of Copolymer Latex

The lattices were prepared by semicontinous emulsion polymerization. The polymerization was carried out in a four necked one litre reactor having a two bladed Teflon (tetrafluoroethelene) coated stirrer and a 25 ml graduated dropping funnel which was immersed in a constant bath at 80 °C and equipped with water condenser. A typical recipe is shown in Table 1. Doubly deionised (DDI) water and emulsifiers were initially charged and maintained under constant agitation of 150 rpm under nitrogen atmosphere for half an hour. The monomers were mixed and then slowly added to stirred solution of surfactant, buffer and DDI water to obtain pre-emulsion. The pre-emulsion was fed to the reactor over a period of 3.5 hours through a dropping funnel at a rate of 0.30 and 0.40 ml/min respectively. No phase separation of pre-emulsion was noticed over the feeding period. The initiator was divided into two portions and the first portion was added to the reactor prior to the addition of the pre-emulsion. Thereafter the second portion of the initiator which was dissolved in deionized water to form a concentrated solution, was added to the reactor concurrently with the pre-emulsion. After the addition of all the ingredients the reaction mixture was further heated for 1hr at 80 °C. After that the reactor content was cooled at 28 °C, it was filtered to remove any residual coagulum and finally the copolymer latex was obtained. Likewise the latices containing different monomer composition of VAc-BuA with 85/15, 75.5/24.5, 70/30 weight percentage were prepared.

Polymer Characterization by IR

The copolymers were precipitated using acetone were washed with methanol and water (1:1 ratio). They were then dried in vacuum oven at 60 °C. These samples were dissolved in tetra hydro furan, filtered and dried. These samples were used for the FTIR analysis using Bruker (Tensor 27) instrument.

Thermal and Mechanical Tests of Dry Polymer Film

Latex films of 0.2–0.5 mm thickness were dried at room temperature in glass petridishes. These films were used for

Table 1.
Copolymer preparation recipe.

Experiment	85/15 (B1)	75.5/24.5 (B2)	70/30 (B3)
Reactor charge			
Deionized water (g)	70	70	70
Dodecyl benzene sulphonate (DS 10) (g)	0.5	0.5	0.5
Ammoniumpersulphate (g)	0.3	0.3	0.3
Monomer feed			
Vinylacetate (g)	153	135.9	126
Butylacrylate (g)	27	44.1	54
DS 10 (g)	0.25	0.25	0.25
Deionized water (g)	105	105	105
Rexol N-300 (g)	9	9	9
Na_2CO_3 (g)	0.12	0.12	0.12
Initiator feed			
Deionized water (g)	22.5	22.5	22.5
Ammoniumpersulphate (g)	1.2	1.2	1.2

Table 2.
Paint formulation.

Ingredients	Weight (g)		
	*PB1	*PB2	*PB3
Water	35	35	35
Wetting agent	0.42	0.42	0.42
Antiskinning agent	0.42	0.42	0.42
Dispersing agent	0.42	0.42	0.42
Preservative	0.42	0.42	0.42
Antifoaming agent	1.34	1.34	1.34
Coalescing solvent	4	4	4
Above ingredients are to be combined in a low speed ball mill for 10 minutes. While stirring the mixture the following ingredients were added			
Kaolin	17.32	17.32	17.32
Calcium carbonate	18.64	18.64	18.64
TiO_2 (Rutile)	44.6	44.6	44.6
Mix the above ingredients at high speed for 20 minutes. While stirring the mixture the following ingredients were added			
Thickening agent	0.74	0.74	0.74
Antifoaming agent	0.92	0.92	0.92
Ammonia (25%)	0.42	0.42	0.42
The above mixture was stirred for 10 minutes at high speed. Then polymer emulsion was added.			
Polymer emulsion	75	75	75

PB1 – Paint formulation using VAc-BuA copolymer (85/15 wt.%).
PB2 – Paint formulation using VAc-BuA copolymer (75.5/24.5 wt.%).
PB3 – Paint formulation using VAc-BuA copolymer (70/30 wt.%).

mechanical characterization before and after ageing for two weeks at room temperature (28 °C).

Tensile measurements were made at room temperature using Universal Testing Machine (Shimadzu, AG-I). The specimen size was according to ASTM D 412-98 a. A cross head speed 50 mm/min was found suitable to cover the entire range of compositions of the polymers.

A differential scanning calorimeter (DSC, Q100, TA instruments) was used to measure the glass transition temperatures of the samples. Indium was used for temperature calibration ($T_m = 156.6\,^{\circ}C$, $\Delta\tilde{H}_m = 28.4$ J/g). The analyses were done in nitrogen atmosphere using standard aluminum pans. 5–8 mg specimens were first cooled to −80 °C and scan was made from −80 °C to 100 °C at a heating rate of 10 °C/min.

Latex Paint Formulation

The paints were made by mixing proportions of latex with various ingredients in the formulation. The VAc-BuA used in this paint (solid content 40%) was prepared by the semicontinuous emulsion polymerization. According to the Table 2 various latex paints were prepared by different monomer composition using, 85/15, 75.5/24.5, 70/30 wt.% VAc-BuA.

Tests for Paint Evaluation

Sample Preparation

Mild steel panels were used for the preparation of tests samples according to BS specification 1449 (6in × 4in). Panels, free from surface imperfection such as rolling marks, scores and corrosion, were thoroughly degreased with trichloroethylene and dried. The panels were then abraded on the test side with 180 grade silicon carbide paper and then wiped with SBPS 40/65 (special boiling point solvent which is the volatile fraction derived from petroleum at the range 40–65 °C) to remove any contaminants. Care should be taken that there should not be any time gap between degreasing and painting. The coated panels were air dried as required without any contamination.[3]

Water Resistance Test

This test was used to assess the resistance towards water. It is sometimes referred to as blister resistance. Blistering was assessed by using photographic standards (ASTM D 714-56). Thermostatically controlled rectangular water bath of capacity 5 litres equipped with mechanical stirring was used.

Salt Spray Test

This test was used to assess corrosion resistance. It was done according to British standards Institution Method BS 3900 standards.

Alkali Resistance Test

Resistance towards atleast three alkali (trisodiumorthophosphate, anhydrous sodiumcarbonate and sodiumhydroxide) was assessed by blistering according to ASTM D 714-56 standards.

Results and Discussion

The films of copolymer latices produced by semi continuous process were smooth for different compositions. The filming ability was better in 85/15 wt.% VAc-BuA latex film.

Copolymer Characterization

IR spectroscopy

Figure 1(a)–(c) shows the IR spectrum of n-Butyl acrylate monomer, Vinyl acetate monomer and VAc-BuA copolymer respectively.

The figures show that C=C stretching absorption in the range 1600–1650 cm^{-1} for the monomers disappeared in the IR spectrum of VAc-BuA copolymer. The C=O stretching absorption in the range 1650–1800 cm^{-1} and C–O stretching absorption in the range 1150–1250 cm^{-1} are present both in

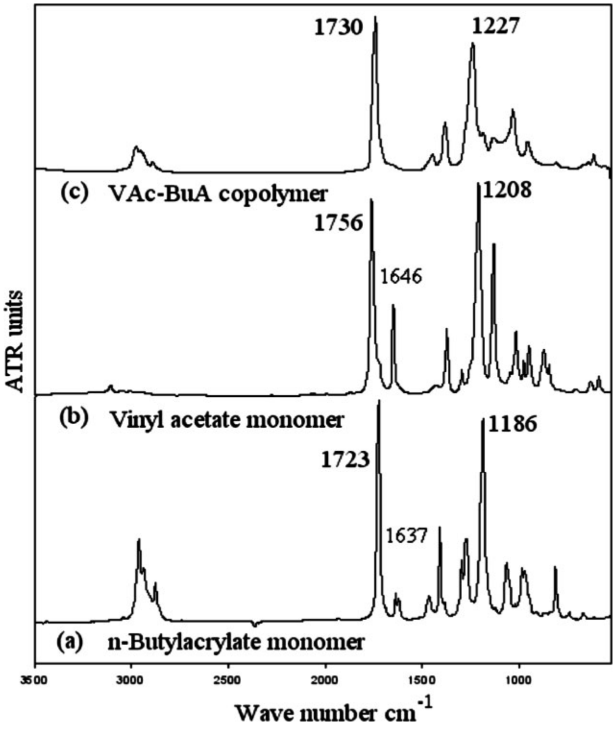

Figure 1.
FTIR spectra of (a) n-butylacrylate, (b) vinyl acetate and (c) VAc-BuA copolymer.

Table 3.
Physical characteristics of VAc-BuA copolymer with different compositions.

Properties	Composition of VAc-BuA copolymer		
	B1	B2	B3
Solid content	40%	40%	40%
pH	6.5	6.3	6.1
Viscosity	600 centipoise	620 centipoise	615 centipose

B1-85/15 wt.% of VAc-BuA, B2-75.5/24.5 wt.% of VAc-BuA, B3-70/30 wt.% of VAc-BuA.

Table 4.
Tensile properties of VAc-BuA copolymer latex films with different molar ratio of monomers.

Property	VAc/BuA copolymer of different compositions		
Molar ratio	B1 (89/11)	B2 (82/18)	B3 (77/23)
Tensile strength (MPa)	9.685	8.778	7.375
Young's modulus (MPa)	34.95	9.395	7.638
Energy to break(j)	0.787	0.242	0.185

the monomers and copolymer. These results show that copolymerization took place between vinyl acetate and butyl acrylate as expected and the functional groups remain unaffected during polymerization. The copolymerization is further confirmed from the single Tg value obtained for the copolymers prepared by semicontinuous emulsion polymerization.[4,5]

Physical Characteristics of Copolymer

Table 3 shows the physical characteristics of the co-polymer of Vinyl acetate with Butyl acrylate.

The Table 3 shows that all the binders possess solid content 40%. Total solid content below 45% was preferable for better performance of paint than higher solid content emulsion. The pH of the latex for the paint preparation should be in the range of 6–8.[1] The pH of prepared latices found to be in the above cited range. Viscosity of the latex has no direct correlation with viscosity of final paint. Low viscosity latices are naturally preferred for easy handling of the paint.

Mechanical Properties of Copolymer

The tensile data are given in Table 4. All the films prepared from the semicontinuous emulsion polymerization process with varying composition show variation in mechanical properties. From Table 4 we observe that tensile strength, Young's modulus, and elongation at break changed significantly for the semicontinuous latex films. It was observed that the sample B_1 has higher tensile strength and Young's modulus than that of the samples B_2 and B_3. This may be due to the homogeneously dispersed morphology corresponding to the copolymer composition of 85/15wt.% VAc-BuA.[4]

Glass Transition Temperature of Copolymer

From Table 5 we observe that each binder B1, B2 and B3 show single glass transition temperature. This single Tg value for B1, B2

Table 5.
T_g values of VAc-BuA copolymerlatex films of different compositions.

Sample name	B1	B2	B3
Glass transition temperature (T_g)	−6.49	−8.3	−9.74

Water resistance test:

Table 6.
Blister formation on the surface.

Time interval	Number and size of the blister			
	PB1	PB2	PB3	Commercial[*]
24 hrs	Nil	Nil	Nil	Nil
4 days	Nil	Nil	Few	Nil
1 week	Nil	Few	Medium	Nil
3 week	Nil	Medium	Medium dense	Few
12week	Few	Dense	Dense	Medium

[*]Commercially available emulsion paint.

Salt spray test:

Table 7.
Blistering assessed by photographs by ASTM standards for salt spray.

Time interval	Number and size of the blister			
	PB1	PB2	PB3	Commercial
48 hrs	Nil	Nil	Nil	Nil
1 week	Nil	Nil	Peeled	Nil
4 week	Nil	Few	Peeled	Few
12 week	Few	Medium dense	Peeled	Medium dense

Alkali resistance test:

Table 8.
Blistering assessed for Na_3PO_4 (75 °C) resistance.

Time interval	Number and size of the blister			
	PB1	PB2	PB3	Commercial
4 hrs	Nil	Nil	Medium	Nil
8 hrs	few	medium	Peeled	few
16 hrs	medium	dense	Peeled	dense
24 hrs	dense	peeled	Peeled	peeled

Table 9.
Blistering assessed for Na_2CO_3(65 °C) resistance.

Time interval	Number and size of the blister			
	PB1	PB2	PB3	Commercial
4 hrs	Nil	few	few	Nil
8 hrs	few	medium	Peeled	few
16 hrs	medium	dense	Peeled	dense
24 hrs	dense	peeled	Peeled	peeled

Table 10.
Blistering assessed for NaOH(28 °C) resistance.

Time interval	Number and size of the blister			
	PB1	PB2	PB3	Commercial
4 hrs	Nil	Few	Medium	Nil
8 hrs	medium	Dense	Peeled	dense
16 hrs	dense	Peeled	Peeled	peeled

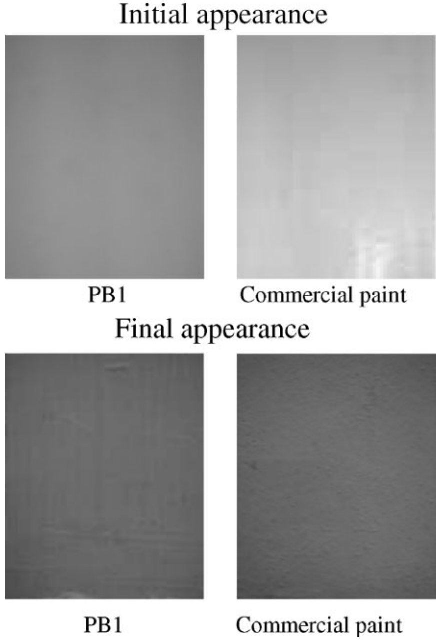

Figure 2.
Photographs showing the paint surface during water resistance test.

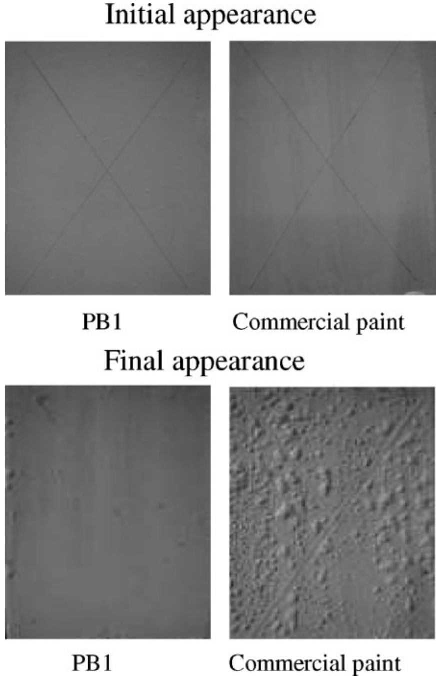

Figure 3.
Photographs showing the paint surface during salt spray test.

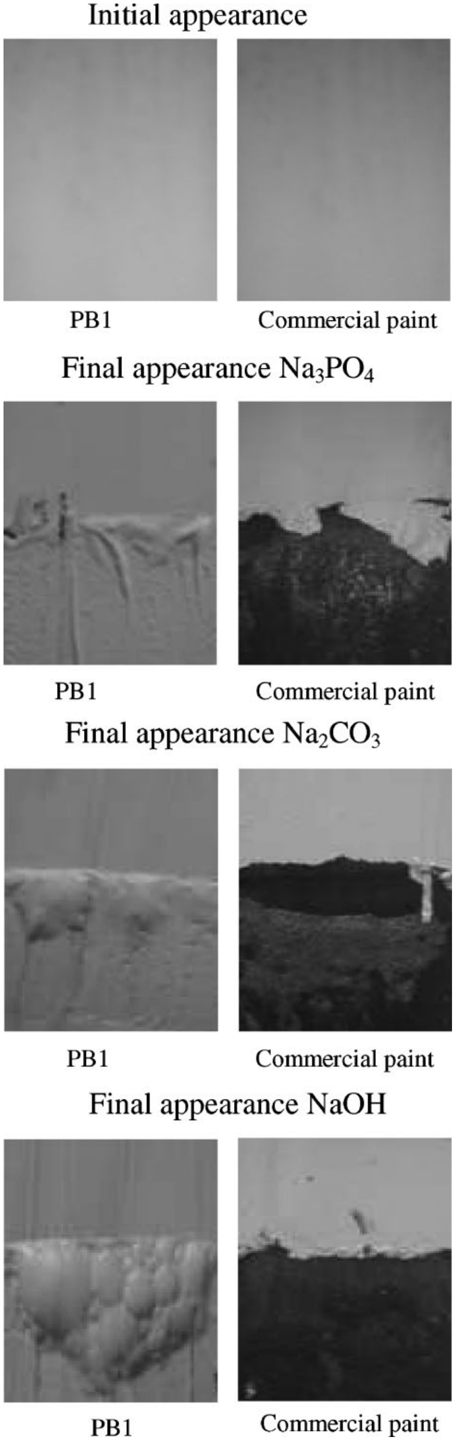

Figure 4.
Photographs showing the paint surface during alkali resistance test.

and B3 indicates that the copolymer formed may be either alternate or random copolymer.[4,5] As per Table 5 the decreasing nature of Tg can be seen by increase of BuA content in the copolymer latex. Tg is found to decrease due to loosening of the VAc polymer chain by the addition of BuA having low Tg (−43 °C). Glass tansition temperature of polymer used in coating industry generally lies between −10 °C and 28 °C.[6]

Tests for Paint Evaluation

The Tables 6–10 shows the results of water resistance, salt spray and alkali resistance tests. The tables show that the paint formulated with 85/15 wt.% of VAc-BuA have good result. The photographs of initial and final specimens of PB1 and commercial samples are shown on the right side of the Table 6–10.

Architectural paints based upon auto oxidisable binders have seeds of degradation within them. The oxidation process does not stop when the film has dried. Oxidation proceeds, giving an increasingly cross linked film. The durability of exterior paint is due to the careful choice of binder which aims to keep the oxidisability of the film to the minimum.[3] Failure of paints may due to either of chemical resistance and optimum mechanical properties or to combinations of them. The binder B1 has minimum oxidisability, high chemical resistance and optimum mechanical properties. Hence B1 shows better performance in paint formulation.

Conclusions

Binder based on vinylacetate and butylacrylate was successfully prepared by semicontinuous emulsion polymerization. The prepared binder was characterized using FTIR and DSC and mechanical properties were also evaluated. Using the aforesaid binder a new formulation for producing paint was prepared and subsequent properties were studied. Out of the different paints prepared, the formulation which made use of the composition 85/15 wt.% of VAc-BuA binder showed good performance in properties such as water resistance, alkali resistance and salt spray tests compared to commercial grade paint.

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